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Synthesis and X-ray structure of neutral Pd(IV) hydride complexes supported by β-ketoimine ligands

Najoua Belhaj Mbarek Elmkacher [a,*], Mongi Ben Amara [b], M'hamed Ali Hamza [c], Faouzi Bouachir [a]

[a] Laboratoire de Chimie de Coordination, Département de Chimie, Faculté des Sciences de Monastir, Avenue de l'Environnement, 5019 Monastir, Tunisia
[b] Laboratoire des matériaux inorganiques, Département de Chimie, Faculté des Sciences de Monastir, Avenue de l'Environnement, 5019 Monastir, Tunisia
[c] Département de Chimie, Faculté des Sciences de Monastir, Avenue de l'Environnement, 5019 Monastir, Tunisia

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ABSTRACT

A series of neutral palladium(IV) hydride complexes supported by β-ketoimine ligands was synthesized. Reaction of dichlorobis(acetonitrile)palladium(II) with β-ketoamines (**1–4**) in dichloromethane at room temperature generated dark red solids of [$PdCl_2$(β-ketoimine)(H)] (**6–9**) in which the central carbon of the ketoimine ligand is σ-bound to the palladium. All the new complexes have been characterized by NMR and IR spectroscopy. The structure of complex(**9**) has been solved by X-ray crystallography.

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1. Introduction

Since the concept of hemilabile bidentate ligands was introduced by Jeffrey and Rauchfuss [1] various combinations of different donors have been studied [2–10].

Ligands of the type O–Y (where Y is N or S) are particularly interesting to mixed-ligand-complex catalytic systems, which are shown to be very effective catalysts in α-olefin and polar olefin polymerization, for example, nickel-based systems [11,12].

Recently β-ketoamine ligands have drawn interest. In their deprotonated form they can be viewed as another potential isoelectronic alternative to cyclopentadienyl anion owing to their chelating ability, planar skeleton and resonance driven high acidity. Although complexes incorporating anionic ligands of this type have been reported [13–19], examples in which the ligand is bound as a neutral donor appear to be rare [15,19,20–27].

Two coordination modes were described in the literature for the β-ketiminate (Scheme 1).

Mode A was adopted for most of the described complexes. Mode B was recently described [26], the essential feature of this type is that the ligand in a binuclear complex is both chelating and bridging.

For the neutral β-ketoamine, only one bonding mode was described (mode C).

On the other hand, hydride complexes of transition metals represent a unique class of compounds which play an exceedingly important role in various fields of chemistry.

Palladium hydrides are of special interest due to their exceptional relevance to catalysis. Perhaps, no other metal can compete with palladium in the ability to catalyze efficiently many useful processes, such as various oxidation, reduction, isomerization, carbonylation, and coupling reactions, aromatic nucleophilic substitution, cyclizations, cycloadditions, and others. In fact, various hydride complexes of palladium have been proposed as key intermediates in diverse Pd catalyzed reactions described in hundreds of experimental papers and several specialized monographs [28–30]. Obviously, the synthesis of palladium hydrides and investigation of their chemical properties represent a special challenge in organometallic chemistry and catalysis.

Vedernikov et al. [31] briefly communicated their striking observations of the oxidative addition of various nonactivated, aliphatic and aromatic C–H bonds to [$(Ph_3P)_2PdX_2$] (X: Cl, Br, I) under exceedingly mild conditions (20–130 °C) (Scheme 2). The process is obviously of exceptional interest.

In a few cases (R: Cy, X, Br, I) the organopalladium(IV) hydrides were isolated in admixtures with the starting Pd(II) complexes. Homogeneous Pd(IV) hydride complexes were not described.

We have prepared previously β-diimine palladium complexes by treatment of neutral β-iminoamine ligands with the zerovalent complex $Pd(dba)_2$ in the presence of the methallyloxyphosphonium salt [32–35].

To the best of our knowledge, however, the reaction of $(CH_3CN)_2PdCl_2$ with neutral β-ketoamine has not yet been reported.

As a continuation of our study [32–35], we have examined this reaction with the hope that new complexes incorporating this ligand as a β-ketoimine tautomer will be prepared.

* Corresponding author. Tel.: +216 73296030; fax: +216 73500278.
E-mail address: najouahaj@yahoo.fr (N.B.M. Elmkacher).

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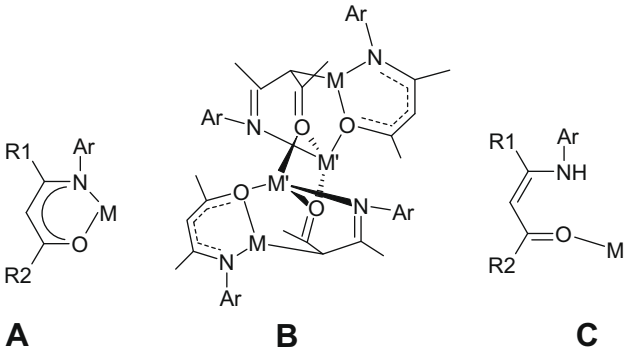
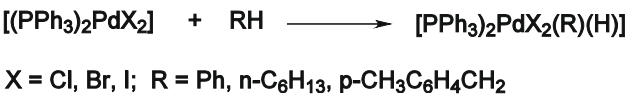


Scheme 1. Coordination modes for the β-ketiminate ligand.



Scheme 2. Oxidative addition of C–H bonds to $[(Ph_3P)_2PdX_2]$.

In this paper we describe a one-pot synthesis of new hydride complexes of palladium(IV) supported by β-ketoimine ligands.

2. Results and discussion

These compounds $[(PhCO)CH(CH_3CNAr)]Pd(H)(Cl)_2$ which are isolated as stable solids, can be easily obtained in high yields by the reaction of the compound $Pd(CH_3CN)_2(Cl)_2$ **5** in methylene chloride in the presence of a β-ketoamine ligand (Scheme 3).

The new complexes **6–9** which are soluble in methylene chloride gave satisfactory analysis and were characterized by ^1H, ^{13}C {1H} NMR and IR spectroscopy.

NMR data for β-ketoamine ligands (**1**–**4**) are consistent with the hydrogen-bridged β-ketoamine.

All ^1H NMR spectra of ligands present a broad signal, which corresponds to the protons of the amine function (N–H). The chemical shift of this proton appears between 12.37 and 12.84 ppm. It is generally very sensitive to concentration, solvent nature and temperature. The protons of the methyl carried by the amino group appear between 1.68 and 2.41 ppm. The vinylic proton appears in the form of singlet between 5.82 and 5.94 ppm.

However the ^1H NMR spectra of these complexes (**6–9**) show a resonance signal around 5.70 ppm which corresponds to the proton of the central carbon, Thus this resonance is located, respectively, at 5.76, 5.75, 5.67 and 5.66 ppm.

We note that there is no signal between 9 and 14 ppm corresponding to the proton of the amine function (N–H). The protons of the methyl group (CH_3–CN) appear between 2.09 and 2.58 ppm.

The presence of the hydride was confirmed by the presence of the signal at −18 ppm which appears as a singlet.

The ^{13}C NMR spectra of β-ketoamines present a signal characteristic of the sp^2 carbon of the ketone function between 188.46 and 188.95 ppm whereas sp^3 carbon of the amine function appears around 163 ppm. Vinylic carbon appears between 92.25 and 94.91 ppm.

The ^{13}C NMR spectra of the complexes present some characteristics, there is no signal around 93 ppm which is characteristic of the vinylic carbon and all the spectra present a resonance around 32 ppm. The imine carbon shows signals between 182.64 and 186.01 ppm. The carbonyl shows signals between 197.98 and 198.77.

The IR spectrum of compounds **6–9** indicated a shift in the C=O stretching frequency (1747, 1759, 1773, 1745) relative to the respectively corresponding stretching frequency in the free ligands 1–**4** (1665, 1598, 1658, 1620).

X-ray single-crystal analysis reveals that compound **9** exhibits some interesting features.

Suitable dark red single crystals of **9** were obtained by crystallization from CH_2Cl_2/*n*-hexane. Complex **9** crystallizes in the monoclinic unit cell $P2_1/c$ group (Table 1).

An ORTEP-plot shown in Fig. 1 confirms the identity of complex **9** (Fig. 1).

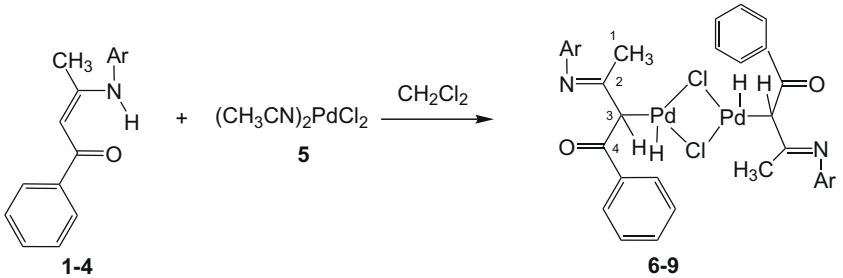
The complex has an unusual structure, the central carbon atom of the β-ketoimine ligand is σ-bound to a $PdCl_2$ fragment. The Pd–C(2) bond length of 2.104(7) Å is in agreement with the known value in the literature for β-diimine related complexes [36].

The palladium atom is in a distorted square planar coordination environment though the hydride was not clearly found in the differential Fourier map. Two coordination sites are occupied by chloride atoms (Cl_1 and Cl_2), the other two sites are defined by the central C atom of the β-ketimine ligand and the hydride ligand. We note that this distortion is illustrated by C(2)–Pd–Cl (2) and C (2)–Pd–Cl(1) angles of 89.5(2)° and 93.2(2)° respectively.

The Pd–Cl(2) bond length of 2.278(2) Å is typical of Pd–Cl distance [37]. The Pd–Cl(1) distance of 2.321(2) Å is indicative of a bridged chloride ligand (Fig. 2). Consequently the complex is a dinuclear compound.

The bond distances within the ligand are consistent with the localized β-ketoimine structure. Selected bond lengths and angles are listed in Tables 2 and 3.

The N–C(1) and O–C(3) bond lengths are typical of double bonds (1.304(9) Å and 1.226(8) Å respectively).



(6) Ar = C_6H_5
(7) Ar = 2-CH_3O-C_6H_4
(8) Ar = 2,4,6-$(CH_3)_3$-C_6H_2
(9) Ar = 2,6-$(iPr)_2$-C_6H_3

Scheme 3. Synthesis of $[(PhCO)CH(CH_3CNAr)Pd(H)(Cl)_2]_2$ complexes.

Table 1
Crystallographic data and structure refinement for **9**.

Empirical formula	$C_{44}H_{54}Cl_4N_2O_2Pd_2$
Formula weight	997.5
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	9.887(2)
b (Å)	14.738(8)
c (Å)	15.583(4)
α (°)	90.00
β (°)	100.88(5)
γ (°)	90.00
Volume (Å^3)	2229.9(14)
Z	4
Calculated density (g cm^{-3})	1.486
Absorption coefficient (mm^{-1})	1.083
F(0 0 0)	1016
Crystal size (mm^3)	0.11 × 0.28 × 0.28
Theta range for data collection	2.10°–24.96°
Limiting indices	$-1 \leqslant h \leqslant 11$, $-1 \leqslant k \leqslant 17$, $-18 \leqslant l \leqslant 18$
Reflections collected/unique	5041/3919 [R(int) = 0.0944]
Completeness to theta = 24.96	100%
Absorption correction	psi-scan
Maximum and minimum transmission	0.8896 and 0.9964
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3919/0/253
Goodness-of-fit (GOF) on F^2	1.022
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0566, wR_2 = 0.1284
R indices (all data)	R_1 = 0.1108, wR_2 = 0.1528
Largest difference peak and hole e Å^{-3}	1.310 and −0.774

$R_1 = \sum(||F_0| - |F_c||)/\sum|F_0|$.
$wR_2 = \left[\sum w(F_0^2 - F_c^2)^2/\sum(F_0^2)^2\right]^{1/2}$, where $w = 1/\left[\sigma^2(F_0^2) + (0.17P)^2\right]$, where $P = (F_0^2 + 2F_c^2)/3$.

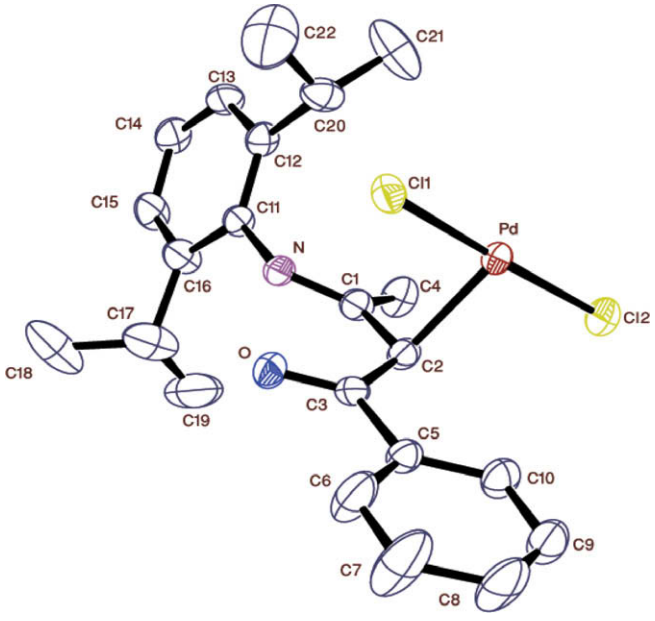


Fig. 1. Perspective ORTEP diagram of complex **9**. Thermal ellipsoids are at 30% probability. Hydrogen atoms are omitted for clarity.

The β-ketoimine ligand core is almost planar, thus the atoms O, C(3), C(2), N are situated in the same plane, whereas the atom C(1) is 0.09 Å out of this plane.

3. Conclusion

We have described a convenient synthetic procedure for the preparation of the new neutral hydride palladium(IV) complexes supported by β-ketimine ligand. The reported results are of particular interest as they contribute to shed light on the one step synthesis of the homogeneous Pd(IV) hydride complexes.

4. Experimental

4.1. General

All manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques.

Methylene chloride and hexane were distilled over P_2O_5. Aniline, 2-methoxyaniline, 2,4,6-trimethylaniline and 2,6-diisopropylaniline were distilled from potassium hydroxide prior to use. $Pd(CH_3CN)_2Cl_2$ [38] and β-ketoamine ligands [34] were prepared according to literature methods. All other reagents were obtained from standard commercial vendors and used as received. NMR spectra were recorded on a Bruker AC-300 spectrometer. H and C chemical shifts are given in ppm and referenced to the residual solvent resonance relative to TMS. Infrared spectra were recorded on a Bruker Victor 22 (Golden Gate Technique).

4.2. General procedure for the preparation of β-ketoamines

The β-ketoamines were prepared by adding 50 mol% excess of the appropriate primary amine directly to the benzoylacetone. The mixture was heated at 100 °C for several hours in the presence of calcium sulfate. The products were purified by crystallization.

4.2.1. 3-N-(phenylamino)-1-phenylbut-2-en-1-one (**1**)

Following the general procedure, from aniline (55 mmol, 5 mL) and benzoylacetone (55 mmol, 8.89 g) was obtained 12.47 g of **1** as a yellow solid after crystallization from hexane. Yield = 83%. m.p. (°C): 111–112. IR (Golden Gate): $\nu_{C=O}$ = 1665 cm^{-1}, ν_{N-H} = 3360 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.41 (s, 3H, (NH)C–CH_3); 5.91 (s, 1H, C*H*CO(Ph)); 7.17–7.95 (m, 10H, H_{arom}); 12.84 (s, 1H, H–N). ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, δ [ppm]): 20.52 (*C*H$_3$–CN); 94.36 (*C*HCO(Ph)); 124.81–140.07 (C_{arom}); 162.32 (*C*–N); 188.71 (*C*=O).

4.2.2. 3-N-(2-methoxyphenylamino)-1-phenylbut-2-en-1-one (**2**)

Following the general procedure, from 2-methoxyphenylamine (44 mmol, 5 mL) and benzoylacetone (44 mol, 7.19 g) was obtained 10.82 g of **2** as a yellow solid after crystallization from hexane. Yield = 92%. m.p. (°C): 142–144. IR (Golden Gate): $\nu_{C=O}$ = 1598 cm^{-1}, ν_{N-H} = 3411 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ [ppm]): 2.06 (s, 3H, (NH)C–CH_3); 3.81 (s, 3H, 2-OCH_3–C_6H_4); 5.83 (s, 1H, C*H*CO(Ph)); 6.84–7.88 (m, 9H, H_{arom}); 12.84 (s, 1H, H–N). ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, δ [ppm]): 20.95 (*C*H$_3$–CN);56.20 (2-OCH$_3$–C_6H_4); 94.91 (*C*HCO(Ph)); 111.73–153.38 (C_{arom}); 162.81 (*C*–N); 188.95 (*C*=O).

4.2.3. 3-N-(2,4,6-trimethylphenylamino)-1-phenylbut-2-en-1-one (**3**)

Following the general procedure, from 2,4,6-trimethylaniline (35 mmol; 5 mL) and benzoylacetone (35 mmol; 5.67 g) was obtained 7.6 g of **3** as a yellow solid. Yield = 78%. m.p. (°C): 113–115. IR (Golden Gate): $\nu_{C=O}$ = 1658 cm^{-1}, ν_{N-H} = 3395 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.68 (s, 3H, (NH)C–CH_3); 2.10 (s, 6H, 2,6-(CH_3)$_2$–C_6H_2); 2.20 (s, 3H, 4-CH_3–C_6H_2); 5.82 (s, 1H, C*H*CO(Ph)); 6.59–7.87 (m, 7H, H_{arom}); 12.37 (s, 1H, N–H). ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, δ [ppm]): 18.61 (4-CH_3–C_6H_2);

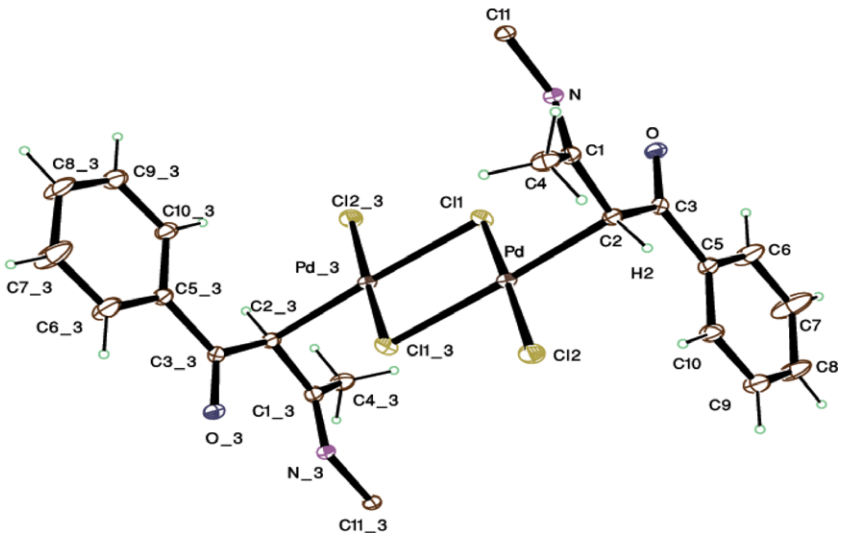


Fig. 2. Perspective ORTEP diagram of complex **9**. Thermal ellipsoids are at 30% probability. Aryl ring are omitted for clarity.

Table 2
Selected interatomic distances (Å).

Pd–C(2)	2.104(7)	C(1)–C(2)	1.457(9)
Pd–Cl(1)	2.321(2)	C(2)–C(3)	1.495(10)
Pd–Cl(2)	2.278(2)	C(1)–C(4)	1.492(10)
N–C(1)	1.304(9)	C(3)–C(5)	1.497(9)
O–C(3)	1.226(8)	N–C(11)	1.459(8)

Table 3
Selected angles (°) for **9**.

N–C(1)–C(4)	119.8(6)	C(1)–N–C(11)	122.4(6)
N–C(1)–C(2)	122.5(7)	C(2)–Pd–Cl(2)	89.5(2)
C(1)–C(2)–C(3)	120.2(6)	C(2)–Pd–Cl(1)	93.2(2)
O–C(3)–C(2)	121.8(6)	Cl(2)–Pd–Cl(1)	176.11(8)
O–C(3)–C(5)	120.7(7)		

19.86 (2,6-(CH_3)$_2$–C_6H_2); 21.36 (CH_3–CN); 92.66 (*C*HCO(Ph)); 122.22–160.26 (C_{arom}); 165.48 (*C*–N); 188.82 (*C*=O).

*4.2.4. 3-N-(2,6-diisopropylphenylamino)-1-phenylbut-2-en-1-one (**4**)*

Following the general procedure, from 2,6-diisopropylaniline (26 mmol; 5 mL), benzoylacetone (26 mmol; 4.9 g) was obtained 8.02 g of **4** as a yellow solid after crystallization from hexane. Yield = 86%. m.p. (°C): 132–133. IR (Golden Gate): $\nu_{C=O}$ = 1620 cm^{-1}, ν_{N-H} = 3386 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ [ppm]): 1.17 (d, 6H, H_3C–iPr, J = 6.9 Hz); 1.23 (d, 6H, H_3C–iPr, J = 6.9 Hz); 1.79 (s, 3H, (NH)C–CH_3); 3.10 (sept, 2H, *H*C–iPr, J = 6.6 Hz); 5.94 (s, 1H, C*H*CO(Ph)); 7.19–7.97 (m, 8H, H_{arom}); 12.64 (s, 1H, H–N). ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, δ [ppm]): 19.93 (CH_3–CN); 22.77 (CH_3–iPr); 24.69 (CH_3–iPr); 28.59 (*C*H–iPr); 92.39 (CHCO(Ph)); 123.63–146.24 (C_{arom}); 165.23 (*C*–N); 188.46 (*C*=O).

4.3. General procedure for the preparation of [(PhCO)CH(CH_3CNAr)]Pd(H)(Cl)$_2$ complexes

In an inert atmosphere, Pd(CH_3CN)$_2$(Cl)$_2$ complex (1 equiv.) was dissolved in 20 cm^3 anhydrous CH_2Cl_2 and β-ketoamine ligands were added (1 equiv.). The dark red solution was stirred at room temperature for 24 h. The supernatant was separated by filtration through a celite filter, and the solvent was removed under vacuum to afford the oil compound. This was washed with hexane (3 × 15 cm^3) and dried in vacuum. The solid was crystallized from methylene chloride/*n*-hexane solution. Yields and spectral data of compounds **6–9** are reported below.

*4.3.1. [(PhCO)CH(CH_3CN(C_6H_5)]Pd(H)(Cl)$_2$(**6**)*

Following the general procedure, from [(PhCO)CH(CH_3CN-(H)(C_6H_5)], (109 mg, 0.457 mmol) and Pd(CH_3CN)$_2$(Cl)$_2$ (0.1 g, 0.457 mmol) was obtained 0.175 g of **6** as a dark red solid after crystallization from a mixture (CH_2Cl_2/*n*-hexane: 1/1).

Yield 92%. IR (Golden Gate): $\nu_{C=N}$ = 1620 cm^{-1}, $\nu_{C=O}$ = 1747 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ [ppm]): −18 (s, 1H, hydride), 2.58 (s, 3H, CH_3–CN), 5.76 (s, 1H, *H*C–Pd), 7.17–8.43 (m, 10H, H_{arom}). ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, δ [ppm]): 23.29 and 23.36 (CH_3–CN), 33.02 and 33.28 (*C*–Pd), 125.20–137.51 (C_{arom}), 182.64 and 182.86 (C=N), 198.59 and 198.77 (C=O).

*4.3.2. [(PhCO)CH(CH_3CN(2–CH_3O–C_6H_4)]Pd(H)(Cl)$_2$ (**7**)*

Following the general procedure, from [(PhCO)CH(CH_3CN(H)(2-CH_3O–C_6H_4)], (0.122 mg, 0.457 mmol) and Pd(CH_3CN)$_2$(Cl)$_2$ (0.1 g, 0.457 mmol) was obtained 0.193 g of **7** as a dark red solid after crystallization from a mixture (CH_2Cl_2/*n*-hexane: 1/1).

Yield 95%. IR (Golden Gate): $\nu_{C=N}$ = 1612 cm^{-1}, $\nu_{C=O}$ = 1759 cm^{-1}. ^{1}H NMR(300 MHz, $CDCl_3$, 25 °C, δ [ppm]): −18 (s, 1H, hydride), 2.56 (s, 3H, CH_3–CN), 3.87 (s, 3H, CH_3O), 5.75 (s, 1H, *H*C–Pd), 7.02–8.46 (m, 9H, H_{arom}). ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, δ [ppm]): 22.76 (CH_3–CN), 31.99 (*C*–Pd), 56.09 (CH_3O), 121.18–152.68 (C_{arom}), 183.04 (C=N), 198.21 (C=O).

*4.3.3. [(PhCO)CH(CH_3CN(2,4,6-(CH_3)$_3$-C_6H_2)]Pd(H)(Cl)$_2$ (**8**)*

Following the general procedure, from [(PhCO)CH(CH_3-CN(H)(2,4,6-(CH_3)$_3$–C_6H_2)], (0.128 g, 0.457 mmol) and Pd(CH_3CN)$_2$-(Cl)$_2$ (0.1 g, 0.457 mmol) was obtained 0.191 g of **8** as a dark red solid after crystallization from a mixture (CH_2Cl_2/*n*-hexane: 1/1).

Yield 91%. IR (Golden Gate): $\nu_{C=N}$ = 1601 cm^{-1}, $\nu_{C=O}$ = 1773 cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, δ [ppm]): −18 (s, 1H, hydride), 2.09 (m, 3H, CH_3–CN), 2.31–2.36 (m, 6H, CH_3–C_6H_2), 2.70 (m, 3H, CH_3–C_6H_2), 5.67 (s, 1H, *H*C–Pd), 6.99–8.46 (m, 7H, H_{arom}). ^{13}C NMR (75.5 MHz, CD_2Cl_2, 25 °C, δ [ppm]): 17.90, 19.38 and 20.82 (CH_3–C_6H_2), 21.73 (CH_3–CN), 31.73 and 31.94 (*C*–Pd), 128.91–139.82 (C_{arom}), 185.76 and 186.01 (C=N), 198.12 and 198.29 (C=O).

*4.3.4. [(PhCO)CH(CH_3CN(2,6-(iPr)$_2$–C_6H_3)]Pd(H)(Cl)$_2$ (**9**)*

Following the general procedure, from [(PhCO)CH(CH_3CN(H)-(2,6-(iPr)$_2$–C_6H_3)], (0.147 g, 0.457 mmol) and Pd(CH_3CN)$_2$(Cl)$_2$ (0.1 g, 0.457 mmol) was obtained 0.215 g of **9** as a dark red solid after crystallization from a mixture (CH_2Cl_2/*n*-hexane: 1/1).

Yield 94%. IR (Golden Gate): $\nu_{C=N}$ = 1583 cm^{-1}, $\nu_{C=O}$ = 1745 cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, δ [ppm]): −18 (s, 1H, hydride), 1.19–1.50 (m, 12H, CH_3–iPr), 2.31 (s, 3H, CH_3–CN), 2.71 (sl, 1H, C*H*–iPr), 4.05 (sl, 1H, C*H*–iPr), 5.66 (s, 1H, *H*C–Pd), 7.28–8.45 (m, 8H, H_{arom}). ^{13}C NMR (75.5 MHz, CD_2Cl_2, 25 °C, δ [ppm]): 22.33 and 22.61 (*C*H_3–CN), 23.05, 23.34, 23.73, 24.90 and 25.57 (*C*H_3–iPr), 28.99 (CH–iPr), 31.65 and 32.83 (*C*–Pd), 124.09–144.91 (C_{arom}), 185.89 (C═N), 197.98 (C═O).

4.4. X-ray crystallographic study

The X-ray crystallographic study of complex 10 was carried out on a CAD4 Enraf–Nonius diffractometer (Mo Kα). Data were collected at 293 K in the range 2–25° and this gave a total of 5041 reflections, yielding 3919 independent values (R_{int} = 0.0944). The structure was solved by direct method and difference Fourier techniques and were refined by full-matrix least-squares analysis. Refinements were based on F^2 and were carried out using all the data (SHELXL-97). All of the non-hydrogen atoms were refined anisotropically. The set of physical and crystallographic characteristics as well as the experimental conditions are listed in Table 1.

Supplementary data

CCDC 683393 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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